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54 Paintable adhesion promoter system for polyvinyl chloride plastisols.

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Description

The present invention relates to plastisols in general and in particular to improved adhesion promoter systems for polyvinyl chloride (PVC) plastisols.

5 The present invention concerns a plastisol composition according to the pre-characterizing portion of claim 1 and a method for making a plastisol composition according to the pre-characterizing portion of claim 8. The present invention also concerns a method for coating to a metal substrate according to claim 15.

Vinyl chloride homopolymers (PVC) and copolymers are widely used for the protection of metallic
10 surfaces against corrosion, for adhering thin sheet metal constructions, and for sealing welded seams, particularly in the automotive industry. Such coatings principally are applied in the form of plasticized vinyl chloride polymers (plastisols) by a variety of techniques. Depending upon the viscosity of the PVC plastisol, its utilization can be characterized as a sealant, caulk, coating, adhesive, or other function.

15 Since resistance to corrosion is a prime prerequisite in dealing with metal parts, the PVC plastisol should adhere to the metal part with a fair degree of tenacity; otherwise, oxidation undercutting would result. Despite the ability to control the texture of the plastisol by suitable fillers and the color by the addition of suitable tinctorial pigments, often the PVC plastisol must be overcoated with a high performance, e.g. acrylic, topcoat, especially in automotive uses of the PVC plastisol. Uniformity in visual appearance dictates such overcoating requirement typically.

20 Another requirement of the PVC plastisol is that it be curable at short, low bake cycles. In fact, successful plastisols and organosols in the automotive industry are being called on today to be curable, dry to the touch, at baking temperatures of less than 149 °C (300 °F), e.g. about 135 °C (275 °F), with oven residence times of about 20–30 minutes. Energy costs dictate such low temperature, short baking cycles. Further, successful plastisol and organisol formulations must be economic and expel a minimum of
25 atmospheric pollutants.

While a variety of adhesion promoters have been proposed for PVC plastisols and organosols, most have suffered from a variety of drawbacks including cost, insufficient film flexibility, or the like. One class of adhesion promoters which appears to exhibit a good balance between cost, flexibility, and low temperature
30 bake characteristics are polyaminoamide–polyimidazoline adhesion promoters, such as set forth in US–A–4 146 520. Such adhesion promoters have enabled the formulation of advantageous PVC plastisols and organosols which can be baked at temperatures as low as about 121 °C (250 °F). Unfortunately, the plastisols and organosols containing such polyaminoamide–polyimidazoline adhesion promoters are not readily overcoated with acid–catalyzed topcoats, especially high performance acid catalyzed acrylic automobile finishes. It is theorized that the amine value of the adhesion promoters interacts and renders
35 ineffectual the acid catalyst in the topcoat, thus resulting in tacky films. While reduction of the level of the adhesion promoter can overcome such topcoat tackiness, loss of adhesion also can occur at such low adhesion promoter levels. Thus, there is a need in the art to enable the utilization of polyaminoamide–polyimidazoline adhesion promoters in low bake PVC plastisol and organisol compositions, yet provide the ability to overcoat such plastisols with acid catalyzed topcoats.

40 The plastisol composition of the present invention is defined according to the characterizing portion of claim 1. The method of making the plastisol composition of the present invention is defined according to the characterizing portion of claim 8. The plastisol composition according to claim 1 is used in a method for coating a metal substrate according to claim 15.

According to a preferred embodiment of the invention the adhesion promoter ranges from between 1
45 and 10 weight parts per 100 weight parts of the vinyl chloride polymer.

For coating a metal substrate according to the present invention the proportion of the secondary plasticizer ranges preferentially from between 10 and 70 weight parts, said primary plasticizer ranges from between 20 and 200 weight parts, and said promoter ranges from between 1 and 10 weight parts, all weight parts based on 100 weight parts of said vinyl chloride polymer.

50 The present invention is addressed to the need in the art to retain advantageous low bake properties of PVC plastisols and their requisite good adhesion to metal, yet still be able to be coated wet–on–dry or wet–on–wet by acid catalyzed topcoats. Accordingly, the present invention is directed to plastisol compositions comprising finely–divided vinyl chloride polymer, filler, a primary plasticizer, and a polyaminoamide–polyimidazoline adhesion promoter. The improvement of the present invention comprises
55 a plasticizer/promoter phase comprising said primary plasticizer, said adhesion promoter, and an effective amount of a secondary plasticizer nonionic solvent effective in solvating said adhesion promoter in said plasticizer/promoter phase wherein the plasticizer/promoter phase is preformed for addition with the remaining ingredients of the plastisol composition. Suitable nonionic secondary plasticizer solvents include

aromatic solvents and polyalkylene glycol ether solvents which are effective in solvating the polyaminoamide - polyimidazoline adhesion promoters.

Another aspect of the present invention involves the method for formulating the improved plastisol compositions wherein the plasticizer/promoter phase comprising the primary plasticizer, the adhesion promoter, and the secondary plasticizer nonionic solvent is pre-formed and then such phase added to the remaining ingredients of the plastisol composition.

Advantages of the present invention include the retention of low bake characteristics of the plastisol and the excellent adhesion characteristics of the plastisol. A further advantage is the ability to overcoat the plastisol wet-on-dry or wet-on-wet with an acid catalyzed topcoat (i.e. "paintability", for present purposes) which is dry to the touch at lower bake temperatures of 121°C - 182°C (250° - 360°F), for example. A further advantage is the ability to exhibit the foregoing advantageous characteristics while retaining the flexibility of controlling the rheological characteristics of the plastisol. A further advantage is an improved plastisol composition which exhibits excellent controlled age characteristics. These and other advantages will be readily apparent to those skilled in the art based upon the disclosure contained herein.

The polyaminoamide - polyimidazoline adhesion promoters are set forth in US - A - 4,146,520. Such adhesion promoters include condensation products formed between a polymerized fatty acid mixture and an excess of polyalkylene polyamine. Such adhesion promoters additionally include the foregoing condensation product further reacted with an aldehyde, a ketone, or an epoxy compound.

While not intending to be bound by theory, it appears that a significant quantity of the adhesion promoter migrates to the surface of the cured plastisol. While such migration does not adversely impair the performance of the plastisol, it does adversely affect the curability of acid catalyzed topcoats which then are applied to the wet (wet-on-wet) or dry (i.e. wet-on-dry) plastisol. It is believed that the amine value of the adhesion promoter reacts with the acid catalyst in the topcoat which means that the topcoat will not be fully cured at the recommended bake temperatures of about 150°C (300°F) or thereabouts. As noted above, such undesirable interaction can be mostly obviated by a reduction of the amount of adhesion promoter in the plastisol, though such reduction compromises the degree of adhesion achievable, so that this alternative is not commercially viable. The same holds true for increasing the amount of acid catalyst in the acid catalyzed topcoat.

One way of viewing the result of the invention is that the adhesion promoter is rendered more compatible or homogeneous in the plastisol so that it does not overconcentrate at the film surface. Accordingly, appropriate secondary plasticizer solvents or diluents should be effective in solvating the polyaminoamide - polyimidazoline adhesion promoters. Next, such secondary plasticizer solvents should be non-ionic. Solvents rich in amine value, for example, should be avoided even though they may effectively solvate the adhesion promoters as such solvents only contribute to the problem being solved. Accordingly, nonionic solvents are recommended.

Suitable nonionic solvents which solvate the adhesion promoter include aromatic solvents and polyalkylene glycol ether solvents. By "solvate", we mean that a clear, stable solution results upon the mixing of the nonionic solvent and the adhesion promoter, typically at room temperature though moderate heating may be employed. Suitable such nonionic solvents include, for example, monoisopropyl biphenyl, diethylene glycol monoethyl ether, diisopropyl biphenyl, phenylxylyl ethane, butylated biphenyl and mixtures thereof. The proportion of the secondary plasticizer solvent is adjusted to accomplish its function in the formulation. Often, this means between 10 and 70 phr (weight parts per 100 weight parts of PVC resin) nonionic solvent is used.

The remaining ingredients in the plastisol are conventional and include finely-divided polyvinyl chloride homopolymers or vinyl chloride copolymers, and often blends thereof. The primary plasticizer most often will be an alkyl phthalate such as dihexyl phthalate (DHP) diisodecyl phthalate (DIDP). Alternatively, the primary plasticizer may be an alkyl adipate (e.g. di(2-ethyl hexyl) adipate). The plasticizer typically will range from 20 to 200 phr (weight parts per 100 weight parts of PVC resin).

Additionally the plastisol will contain a filler for control of rheology, control of cost, and the like. Suitable fillers include, for example, calcium carbonate, glass (including hollow glass spheres), talc, chalk, barium sulfate, and the like. The fillers certainly affect paintability of the plastisol, though with the invention more flexibility in filler utilization is gained. The proportion of filler can range up to about 300 phr and the optimum will vary depending upon the type of PVC and plasticizer, and the rheology desired. Finally, thixotropic agents can be added to achieve certain plastisol rheologies and such agents include, for example, fumed silica, bentonite, metallic fatty acid soaps. Thixotropic agents typically are added in the range of about 1 - 5 phr.

In order to maximize the paintability of the plastisol (i.e. ability to coat the plastisol with an acid catalyzed topcoat), it has been determined that a pre-blend of adhesion promoter, primary plasticizer, and

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nonionic secondary plasticizer solvent should be made. Such plasticizer/promoter blend then is added to the remaining ingredients for forming the plastisol. Apparently, the formation of the plasticizer/plastisol blend is more effective in compatibilizing the adhesion promoter in the plastisol or "pushing" the plasticizer into the PVC particles. Regardless of the mechanism involved, it has been determined that paintability of plastisol becomes a routine achievement when the plasticizer/promoter blend is initially formed in making the plastisol composition.

The plastisol is dryable or curable at very low bake temperatures ranging on down to 121° - 135°C (250° - 275°F). The plastisol either can be baked and then topcoated (wet-on-dry) or the plastisol can be applied followed by the topcoat wherein both coatings then are cured in a single bake (wet-on-wet). In automotive applications, the plastisol typically is drawn down or applied onto a metal substrate which has been primed with a corrosion-inhibiting coating. Typical topcoats include high performance acrylic topcoats which are cured by conventional acid catalysts.

The following examples show how the present invention has been practiced but should not be construed as limiting. All percentages and proportions are by weight unless expressly indicated.

EXAMPLES

EXAMPLE 1

The efficacy of polyaminoamide - polyimidazoline adhesion promoters in PVC plastisol formulations was demonstrated on the following general formulation.

TABLE 1

Ingredient*	Amount (wt. - parts)
Occidental 6482 (regist. TM)	60
Borden VC265 (regist. TM)	40
Dihexyl phthalate (DHP)	62.5
Diisodecyl phthalate (DIDP)	62.5
CaCO ₃	250

* Occidental 6482 - A medium molecular weight PVC homopolymer, inherent viscosity 1.07 (ASTM D - 1243), K Value (Fikentscher) 71, specific gravity 1.414 (ASTM D - 792), gelation temperature 73°C (163°F), 100% passes through a 0.044 mm opening size (325 mesh) sieve, Occidental Chemical Corp., Pottstown, Pa.
Borden VC265 - PVC copolymer plastisol blending resin containing 4% vinyl acetate, 33 - 40 µm avg. particle size powder, Borden, Inc., Columbus, Ohio.
CaCO₃ - Atomite brand CaCO₃, 3 µm mean particle size, Thompson, Weinman and Company, Cartersville, Georgia.

Varying levels of adhesion promoter were utilized as follows:

TABLE 2

Formulation No.	Wt. Parts
204 - 65 - 1	10.17
204 - 65 - 2	7.13
204 - 65 - 3	4.75
204 - 65 - 4	3.56
204 - 65 - 5	2.38
204 - 65 - 6	1.19
204 - 65 - 7	0.59

The adhesion promoter was Euretek (registered TM) 580 polyaminoamide adhesion promoter (amine value of 190, manufactured under US - A - 4,146,520, Sherex Chemical Company, Inc., Dublin, Ohio).

Brookfield viscosity measurements were taken on each formulation initially and thereafter at various intervals of time. The following data was recorded.

TABLE 3
Viscosity $mPa \cdot s$

No.	RPM	Initial	3 days	7 days	17 days	24 days	32 days	45 days
1	2.5	154,800	267,200	350,400	334,400	348,800	339,200	324,800
	5	99,400	184,800	249,600	254,400	255,200	244,800	232,800
	10	66,600	125,600	174,800	177,200	178,800	176,400	165,600
	20	47,350	91,800	129,000	130,600	133,000	134,600	125,600
	R yield	3.27 2,770	2.91 4,120	2.72 5,040	2.56 4,000	2.62 4,680	2.52 4,720	2.59 4,500
2	2.5	143,200	283,200	302,400	304,000	272,000	267,200	275,200
	5	91,600	188,800	199,200	209,600	175,200	177,600	185,300
	10	59,300	122,800	130,000	138,800	117,600	119,600	124,300
	20	40,800	85,600	90,800	97,400	84,800	87,200	90,800
	R yield	3.58 2,580	3.31 4,720	3.33 5,160	3.12 4,720	3.21 4,840	3.06 4,480	3.03 4,480
3	2.5	214,400	276,800	312,000	313,600	324,800	262,400	244,800
	5	137,600	171,200	192,800	197,600	205,600	164,800	152,900
	10	87,200	106,400	120,400	126,400	134,800	105,600	98,400
	20	57,200	69,200	78,000	85,800	93,800	72,600	65,400
	R yield	3.75 3,840	4.00 5,280	4.00 5,960	3.66 5,800	3.46 5,960	4.47 4,880	3.71 4,600

TABLE 3 (continued)
Viscosity $mPa \cdot s$

No.	RPM	Initial	3 days	7 days	17 days	24 days	32 days	45 days
4	2.5	228,800	320,000	342,400	328,000	307,200	270,400	276,800
	5	147,200	200,800	212,800	203,200	189,600	168,800	173,600
	10	93,600	124,800	133,200	127,600	118,400	105,600	109,600
	20	61,200	80,600	88,400	83,600	78,400	70,200	73,600
	R yield	3.74 4,080	3.97 5,960	3.87 6,480	3.92 6,240	3.92 5,880	3.85 5,080	3.59 5,000
5	2.5	275,200	347,200	315,200	328,000	310,400	289,600	276,800
	5	177,600	216,800	189,600	202,400	192,000	178,400	173,600
	10	113,200	134,000	114,000	124,800	119,200	109,600	109,200
	20	73,200	85,800	73,600	80,400	76,800	71,400	72,800
	R yield	3.76 4,880	4.05 6,520	4.28 6,280	4.08 6,280	4.04 5,920	4.06 5,560	3.80 5,160
6	2.5	345,600	398,400	361,600	342,400	360,000	342,400	318,400
	5	245,600	246,400	224,000	208,800	218,400	209,600	197,600
	10	158,400	150,800	136,400	127,200	131,600	126,800	120,600
	20	99,800	93,600	84,800	78,800	82,200	78,800	75,600
	R yield	3.46 5,000	4.26 7,600	4.26 6,880	4.35 6,680	4.38 7,080	4.35 6,640	4.21 6,040

TABLE 3 (continued)

No.	RPM	Initial	Viscosity in $P_{a.s}$					45 days
			3 days	7 days	17 days	24 days	32 days	
7	2.5	387,200	449,600	420,700	424,000	414,400	392,000	395,200
	5	274,400	276,800	250,400	253,600	247,200	231,200	235,200
	10	171,200	165,200	147,200	150,400	146,800	137,200	140,000
	20	104,800	98,800	90,000	91,400	88,800	82,600	86,200
	R	3.69	4.55	4.68	4.64	4.67	4.75	4.59
	yield	5,640	8,640	8,520	85,20	8,360	8,040	8,000

* Spindle # 6 for 204-65-1 and 2, and Spindle #7 for all other samples.

R is a measure of the degree of thixotropy and is calculated by dividing the viscosity at 2.5 rpm by the viscosity at 20 rpm.

Yield is a measure of the force required to move the plastisol (thickness of the plastisol) and is calculated as follows:

$$\frac{(2)(2.5 \text{ rpm}) (\text{Viscosity at } 2.5 \text{ rpm} - \text{Viscosity at } 5 \text{ rpm})}{100}$$

Advantageously, the viscosity should stabilize over time. The above - tabulated data demonstrates such viscosity stability.

Each formulation was drawn down (0.50 mm (0.020 inch) coating) on primed steel panels (Uni - Prime coated panels, PPG Industries, used in all examples) and baked for 20 minutes at 121° C. Each coating had good adhesion to the panels except for 204 - 65 - 7, indicating that the promoter level was too low.

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The coated panels then were coated with a white enamel paint (an automotive topcoat based on melamine and a hydroxyl-acrylic resin with an acid catalyst, supplied by PPG Industries, Pittsburgh, Pa.) The topcoated panels were baked at 121 °C for 30 minutes. All samples were slightly tacky and eventually intercoat adhesion was lost (about 50 days). This demonstrates the difficulties encountered in curing an acid catalyzed topcoat over a primer high in amine value. Thus, while metal adhesion and controlled age viscosity were good, paintability was lacking.

EXAMPLE 2

Plasticizer studies extended to various blends in order to retain control age viscosity but improve paintability. The basic formulation studied was as follows:

TABLE 4

Ingredient*	Amount (wt. - parts)
Occidental 6482™	60
Borden VC265™	40
CaCO ₃	100
Talc	20
Silica	1
Euretek™ 580 promoter	3.21phr
Talc - Mistron ZCS grade talc, Cypress Industrial Minerals	
Silica - Cab - O - Sil® brand fumed silica, Cabot Corporation.	
Promoter - phr is weight parts per hundred weight parts of PVC.	

The various plasticizer/promoter phases evaluated are set forth below:

TABLE 5

Formulation No. 204 - 88 (wt. - parts)						
Ingredient	1	2	3	4	5	6
DIHP	50	50	50	50	50	50
DHP	10	20	25	50	50	100
Monoisopropyl biphenyl	40	30	25	- -	- -	40

In formulations 1-3 and 5, the promoter was added to the plasticizer mix slightly warmed until homogeneous. In formulations 4 and 6, the promoter was added after the plastisol was made. Age viscosity measurements were taken as set forth below.

TABLE 6
Viscosity (mPa.s.)

No.	RPM	Initial	1 day	4 days	11 days	22 days	34 days
1	2.5	217,600	188,800	273,600	236,800	251,200	244,800
	5	128,800	113,600	179,200	154,400	172,000	174,400
	10	79,600	69,600	111,600	101,200	119,600	118,800
	20	50,800	46,800	74,400	69,000	84,200	85,800
	R yield	4.28 4,440	4.03 3,760	3.68 4,720	3.43 4,120	2.98 3,960	2.85 3,520
2	2.5	224,000	212,800	212,400	300,800	304,000	308,800
	5	132,800	126,400	165,600	201,600	212,000	211,200
	10	80,800	77,600	105,200	141,600	150,400	148,800
	20	50,800	49,400	69,600	103,400	115,800	117,400
	R yield	4.41 4,560	4.31 4,320	3.77 4,840	2.91 4,960	2.63 4,600	2.63 4,880
3	2.5	220,800	192,000	241,600	246,400	275,200	275,200
	5	122,400	115,200	148,000	153,600	172,800	180,800
	10	73,200	70,400	93,600	97,200	113,200	25,200
	20	46,000	45,600	63,600	65,600	77,200	88,800
	R yield	4.80 4,920	4.21 3,840	3.80 4,680	3.76 4,640	3.56 5,120	3.10 4,720

TABLE 3 (continued)
Viscosity (mPa.s.)

No.	RPM	Initial	1 day	4 days	11 days	22 days	34 days
4	2.5	217,600	214,400	227,200	235,200	233,600	246,400
	5	131,200	128,800	139,200	140,800	139,200	150,400
	10	81,600	79,600	85,600	86,000	86,800	95,200
	20	51,400	50,800	54,600	56,200	56,400	63,400
	R yield	4.23 4,320	4.22 4,280	4.16 4,400	4.19 4,720	4.14 4,720	3.89 4,800
5	2.5	230,400	204,800	214,400	212,800	217,600	217,600
	5	139,200	125,600	130,400	128,800	131,200	132,800
	10	85,600	78,400	81,600	79,200	81,600	82,400
	20	53,800	50,800	52,600	51,200	51,600	53,400
	R yield	4.28 4,560	4.03 3,960	4.08 4,200	4.16 4,200	4.22 4,320	4.07 4,240
6	2.5	193,600	204,800	225,600	196,800	249,600	254,400
	5	124,800	128,800	138,400	122,400	156,800	161,600
	10	75,200	78,400	85,600	74,800	08,000	109,600
	20	46,200	50,000	54,600	51,600	64,800	70,600
	R yield	4.19 3,440	4.09 3,800	4.13 4,360	3.81 3,720	3.85 4,640	3.32 4,640

Spindle # 7 for all samples.

Coatings on primed steel panels 0.50 mm (0.20 inch thickness) were baked at 121 °C for 20 minutes. All films adhered well except No. 204 - 88 - 5 (control). The acid catalyst topcoat of Example 1 was applied over the cured plastisols and baked at 121 °C for 30 minutes (wet - on - dry). Nos. 1 - 3 were dry while Nos. 4 and 5 were slightly tacky. Thus, the paintability of the plastisol had been improved by the addition of the secondary plasticizer solvent, monoisopropyl biphenyl. The amount of secondary plasticizer solvent appeared to be a bit low in Nos. 2 and 3, so that the formulation of this example appears to require at least about 40 weight parts of monoisopropyl biphenyl in order for paintability to be realized.

EXAMPLE 3

The basic formulation of Example 2 (Table 4) was studied again at higher levels of monoisopropyl biphenyl: 50 wt. -parts for 204-96-1 and 70 wt. -parts for 204-96-2. Again, the technique of blending the adhesion promoter into the plasticizer blend prior to making the plastisol was utilized. The age viscosity data recorded is set forth below.

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TABLE 7
Viscosity (mPa.s)

No.	RPM	Initial	1 day	6 days	14 days	21 days	30 days	45 days
1	2.5	142,000	161,600	172,000	174,400	815,600	195,200	180,000
	5	86,600	99,200	106,400	115,200	120,800	126,400	111,400
	10	55,100	62,900	67,800	74,400	78,800	84,000	71,700
	20	36,350	41,650	46,200	48,200	52,800	56,600	47,100
	R yield	3.91 2,770	3.88 3,120	3.72 3,280	3.62 2,960	3.52 3,240	3.45 3,440	3.77 3,430
2	2.5	174,400	118,400	105,600	124,800	134,400	140,800	163,200
	5	115,600	105,600	98,400	101,600	104,400	123,200	122,400
	10	74,700	88,400	90,400	96,400	98,800	99,200	101,600
	20	48,300	64,800	69,200	79,200	81,600	77,400	82,400
	R yield	3.61 2,940	1.83 640	1.33 360	1.58 1,160	1.65 1,000	1.82 880	1.98 2,040

Spindle # 6 for Initial, 1 day, and 6 days for No. 1 and for Initial for No. 2;

Spindle #7 for all other samples.

Each plastisol exhibited good adhesion to the steel panels (bake protocol of 121 °C for 20 minutes). The acid catalyzed topcoat of Example 1 was applied wet-on-dry and wet-on-wet with baking at 121 °C for 30 minutes for both. The topcoat was not tacky for both systems. Note the slightly increased secondary solvent levels used compared to Example 2. Thus, the ability to achieve paintability while retaining adhesion to metal has been achieved.

EXAMPLE 4

The following formulations were studied.

TABLE 8

Formulation No. 204 - 147		
Ingredient	(wt - parts)	
	1	2
Occidental 6482™	60	60
Borden VC265™	40	40
CaCO ₃	200	200
Talc	10	10
DIDP	60	60
Monoisopropyl biphenyl	40	40
Euretek 580 promoter™	3	3

The plasticizer/promoter blend of No. 1 was mixed at room temperature and then added to the plastisol. The plasticizer/promoter blend of No. 2 was mixed at 72°C and then added to the plastisol. The effects of temperature during the formulating, thus, were being studied.

Both plastisols were coated on steel panels and subjected to wet-on-dry and wet-on-wet top-coating as in Example 3. No apparent performance difference between the two formulations observed.

EXAMPLE 5

Various secondary plasticizer solvents were studied utilizing the basic formulation of Example 2. The various plasticizer blends studied are set forth below:

TABLE 9

Formulation No. 204 - 98			
Ingredient	(wt. - parts)		
	1	2	3
DIDP	50	50	50
DHP	10	10	10
Butylated biphenyl	40	--	--
Diisopropyl biphenyl	--	40	--
Phenylxylyl ethane	--	--	40

The plasticizer/promoter blends were made and then added to the remaining ingredients, as described above. Age viscosity data are set forth below.

TABLE 9
Viscosity (cm²/s)

No.	RPM	Initial	6 days	14 days	30 days	45 days
1	2.5	212,800	198,400	190,400	201,600	185,600
	5	147,200	120,800	113,600	121,600	111,200
	10	96,000	74,800	70,400	75,600	69,600
	20	62,400	48,200	45,400	50,600	45,000
	R yield	3.41 3,280	4.12 3,880	4.19 3,840	3.98 4,000	4.12 3,720
2	2.5	259,200	225,600	206,400	214,400	206,400
	5	172,000	136,800	124,800	131,200	123,200
	10	106,800	84,800	76,400	82,000	77,200
	20	68,200	54,400	50,600	55,400	50,800
	R yield	3.80 4,360	4.15 4,440	4.08 4,080	3.87 4,160	4.06 4,160
3	2.5	171,200	195,200	195,200	188,800	190,400
	5	143,200	125,600	120,800	117,600	121,600
	10	98,800	78,000	75,600	71,200	74,800
	20	64,000	51,600	50,800	47,200	49,600
	R yield	2.68 1,400	3.78 3,480	3.84 3,720	4.00 3,560	3.84 3,440

Spindle # 7 for all samples.

The formulations were coated and cured on steel panels (121 °C for 20 minutes) and topcoated wet-on-dry and wet-on-wet as in the previous examples. Again, good adhesion to the substrates was achieved. The wet-on-dry topcoats also were tack free while the wet-on-wet topcoats were very slightly tacky. Thus, the efficacy of additional aromatic secondary plasticizer solvents is demonstrated.

EXAMPLE 6

The following formulations were made as described above.

TABLE 10

Formulation no. 204 - 116				
Ingredient	(wt. - parts)			
	1	2	3	4
Occidental 6482™	60	60	60	60
Borden VC265™	40	40	40	40
CaCO ₃	200	200	200	200
DIDP	60	60	60	30
DHP	--	--	--	30
Euretek 580 promoter™	5	3	3	3
Monoisopropyl biphenyl	40	40	--	--
Diethylene glycol monoethyl ether	--	--	40	40

Control age viscosity data recorded is set forth below.

TABLE II
Viscosity (mPa.s)

No.	RPM	Initial	3 days	14 days	25 days	31 days
1	2.5	211,200	206,400	233,600	241,600	284,800
	5	171,200	196,800	220,800	215,200	237,600
	10	115,200	153,200	175,600	164,400	180,800
	20	79,600	106,600	126,400	121,600	137,600
	R yield	2.65 2,000	1.94 480	1.85 640	1.99 1,320	2.07 2,360
2	2.5	219,200	256,000	262,400	278,400	281,600
	5	144,000	211,200	228,800	246,400	231,200
	10	98,400	153,600	169,200	180,000	172,400
	20	60,600	109,400	115,400	132,400	124,200
	R yield	3.62 3,760	2.34 2,240	2.27 1,680	2.10 1,600	2.27 2,520
3	2.5	6,240	15,520	33,200	33,200	34,400
	5	5,040	12,080	23,200	25,000	25,600
	10	4,320	9,760	17,800	20,400	20,500
	20	3,860	8,120	14,600	16,550	16,750
	R yield	1.62 60	1.91 172	2.27 500	2.00 410	2.05 440

TABLE 11 (continued)
Viscosity (mPa.s)

No.	RPM	Initial	3 days	14 days	25 days	31 days
4	2.5	5,440	15,360	32,800	40,400	44,800
	5	4,480	12,240	25,000	31,400	34,800
	10	3,840	10,160	20,200	25,600	28,100
	30	3,340	8,920	17,050	21,950	23,850
R yield		1.63 48	1.72 156	1.92 390	1.84 450	1.88 500

Spindle # 7 for No. 1 and No. 2; Spindle # 5 for Initial and 3 days for No. 3 and No. 4;

Spindle # 6 for remaining samples.

The plastisols were coated on panels (121 °C for 20 minutes) and topcoated wet-on-dry as described in the previous examples. Again, good substrate adhesion was achieved. The topcoats were dry for Nos. 2, 3, and 4, and only very slightly tacky for No. 1. Again, the low temperature paintability of the inventive plastisols is demonstrated.

EXAMPLE 7

Additional studies of the ether secondary plasticizer solvent were undertaken on the following formulations.

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TABLE 12

Formulation No. 204 - 98			
Ingredient	(wt. - parts)		
	1	2	3
Occidental 6482™	60	60	60
Borden VC265™	40	40	40
CaCO ₃	200	200	200
DIDP	90	80	105
Diethylene glycol monoethyl ether	10	20	20
Euretek 580 promoter™	3	3	3

Control age viscosity data is set forth below.

TABLE 13
Viscosity (mPa.s)

No.	RPM	Initial	1 day	3 days	10 days	21 days	24 days
1	2.5	128,800	170,400	249,600	283,200	267,200	254,400
	5	78,600	104,000	151,200	177,600	167,200	158,400
	10	50,200	66,400	96,400	114,400	108,400	102,400
	20	33,950	44,900	63,200	79,200	74,800	70,800
	R yield	3.79 2,510	3.80 3,320	3.95 4,920	3.58 5,280	3.57 5,000	3.59 4,800
2	2.5	65,600	98,400	135,200	161,200	170,800	164,800
	5	40,200	59,400	82,400	96,800	106,600	100,200
	10	25,600	38,200	52,600	63,800	69,700	64,900
	20	17,700	25,800	36,000	45,050	47,350	44,950
	R yield	3.71 1,270	3.82 1,950	3.76 2,640	3.58 3,220	3.61 3,210	3.67 3,230
3	2.5	35,680	59,520	82,720	109,600	105,600	101,200
	5	20,880	35,360	48,960	65,200	63,600	60,400
	10	18,000	22,080	30,240	40,300	39,600	37,300
	20	8,620	14,500	19,600	26,300	26,200	24,600
	R yield	4.14 740	4.10 1,208	4.22 1,688	4.17 2,220	4.03 2,100	4.11 2,040

Spindle #6 for No. 1 and No. 2; Spindle #5 for No. 3.

Good adhesion to steel panels again was achieved. The wet-on-dry topcoats (121 °C for 30 minutes) also were dry. The efficacy of the ether secondary plasticizer solvent again is demonstrated.

EXAMPLE 8

Formulation No. 204-118-1 (Example 7) was evaluated again along with an equivalent formulation which used a different adhesion promoter (No. 2) at the same level: Euretek® 555 polyaminoamide-
5 polyimidazoline adhesion promoter (amine value of 380; Gardner color of 12; 8.1 lb/gal. at 82.2 °C; Viscosity profile (Brookfield LVT, spindle 34) of 17,000 mPa·s at 43.3 °C, 13,000 mPa·s at 48.9 °C, 9,000 mPa·s at 54.5 °C, 4,000 mPa·s at 60.0 °C, and 2,800 mPa·s at 65.6 °C; Sherex Chemical Company, Inc., Dublin, Ohio). The control age viscosity data recorded is set forth below.

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TABLE 14
Viscosity. (mP.s.)

No.	RPM	Initial	1 day	3 days	10 days	21 days	24 days
1	2.5	128,800	170,400	249,600	283,200	267,200	254,400
	5	78,600	104,000	151,200	177,600	167,200	158,400
	10	50,200	66,400	96,400	114,400	108,400	102,400
	20	33,950	44,900	63,200	79,200	74,800	70,800
	R yield	3.79 2,510	3.80 3,320	3.95 4,920	3.58 5,280	3.57 5,000	3.59 4,800
2	2.5	130,800	145,600	185,600	154,800	154,800	
	5	82,000	87,800	93,600	94,600	95,800	
	10	52,700	55,700	59,800	61,400	62,600	
	20	35,650	37,900	41,950	42,600	43,800	

See Example 7 for No. 1; Spindle # 6 for No. 2.

Panel coatings and wet-on-dry acid catalyzed topcoats were applied as in the previous examples.
 55 Good panel adhesion was achieved. The topcoat on Formulation No. 204-118-1 was dry while the topcoat on Formulation No. 204-126-2 was only slightly tacky.

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EXAMPLE 9

The following formulations were made:

TABLE 15

Formulation No. 204 - 120			
Ingredient	(wt. - parts)		
	1	2	3
Occidental 6482™	60	60	60
Borden VC265™	40	40	40
CaCO ₃	200	200	200
DIDP	90	80	55
Diethylene glycol monoethyl ether	10	20	20
Euretek 580 promoter™	3	3	3

Control age viscosity data is set forth below.

TABLE 16

Viscosity (mPa•s)					
No.	RPM	Initial	1 day	10 days	21 days
1	2.5	108,800	158,400	334,400	318,400
	5	66,600	96,800	212,800	203,200
	10	43,300	61,600	137,600	131,200
	20	30,000	41,600	92,800	90,800
	R	3.63	3.81	3.60	3.51
	yield	2,110	3,080	6,080	5,760
2	2.5	20,400	44,000	225,600	249,600
	5	13,400	27,600	136,800	150,400
	10	10,200	18,900	86,800	10,800
	20	7,850	13,800	56,600	71,200
	R	2.60	3.19	3.99	3.51
	yield	350	820	4,440	4,960
3	2.5	22,800	40,000	313,600	304,000
	5	19,000	32,200	217,600	202,400
	10	16,300	26,100	110,400	137,600
	20	14,700	22,950	81,400	102,800
	R	1.55	1.83	3.85	2.96
	yield	190	490	4,800	5,080
Spindle #6 for Initial and 1 day; Spindle #7 for all other samples.					

Panel and topcoat testing revealed that good panel adhesion still was present but that the wet-on-dry topcoats (121 °C for 30 minutes) were slightly tacky. The reason for the diminution in performance of this butyl ether solvent compared to the ethyl ether version is not understood presently.

EXAMPLE 10

The following formulations were made.

5	Formulation No. 204						
	Ingredient*	(wt. - parts)					
		103 - 1	103 - 2	105 - 1	105 - 2	138 - 1	138 - 2
10	Occidental 6482™	60	60	60	60	60	60
	Borden VC265™	40	40	40	40	40	40
	CaCO ₃	100	100	100	100	200	200
	Talc	20	20	20	20	--	--
	Silica	1	1	1	1	--	--
15	DIDP	30	20	50	30	90	80
	DHP	30	20	25	30	--	--
	Monoisopropyl biphenyl	20	30	--	--	--	--
	Propylene glycol dibenzoate	20	30	--	--	--	--
	Ethyl toluene sulfon amide	--	--	25	40	--	--
20	(ortho and para isomer mixture)						
	Ethoxylated nonyl phenol	--	--	--	--	10	20

* Euretek 580™ promoter added at 1% by weight in all formulations. Ethoxylated nonyl phenol - Igepal® CO - 630 nonylphenoxy poly(ethyleneoxy) ethanol, GAF Corporation.

25 While the aromatic ester, the sulfonamide, and the nonyl phenol solvents all solvated the adhesion promoter, wet-on-dry paintability was lacking. Ester solvents appear not to be beneficial due to postulated undesirable interaction with other ingredients. The sulfonamide solvent adds more amine value to the plastisol which is not desirable for achieving cure of the acid catalyzed topcoat. The ethoxylated nonyl
30 phenol solvent should have functioned properly according to current understanding of the invention. Perhaps different levels or degrees of ethoxylation will enable this solvent, to function as plastisol.

Claims

- 35 1. A plastisol composition comprising finely-divided vinyl chloride polymer, filler, a primary plasticizer, and a polyaminoamide-polyimidazoline adhesion promoter, wherein for overcoating said plastisol with an acid catalyzed topcoat said composition comprises a plasticizer/promoter phase comprising said primary plasticizer and said adhesion promoter, characterized in that said plasticizer/promoter phase comprises in addition an effective amount of a secondary plasticizer nonionic solvent effective in
40 solvating said adhesion promoter in said plasticizer/promoter phase, said plasticizer/promoter phase being preformed for addition with the remaining ingredients of the plastisol composition.
2. The plastisol composition of claim 1 characterized in that said secondary plasticizer nonionic solvent ranges from between 10 to 70 weight parts per 100 weight parts of said vinyl chloride polymer.
- 45 3. The plastisol composition of claim 1 characterized in that said primary plasticizer ranges from between 20 and 200 weight parts per 100 weight parts of said vinyl chloride polymer.
4. The plastisol composition of claim 1 characterized in that said adhesion promoter ranges from between
50 1 and 10 weight parts per 100 weight parts of said vinyl chloride polymer.
5. The plastisol composition of claim 1 characterized in that said secondary plasticizer nonionic solvent is selected from the group consisting of monoisopropyl biphenyl, diethylene glycol monoethyl ether, diisopropyl biphenyl, phenylxylyl ethane, butylated biphenyl, and mixtures thereof.
- 55 6. The plastisol composition of claim 1 characterized in that it contains more than one of said vinyl chloride polymer.

7. The plastisol composition of claim 1 characterized in that it additionally comprises a thixotropic agent ranging from between 1 and 5 weight parts per 100 weight parts of said vinyl chloride polymer.
8. A method for making a plastisol composition which comprises:
 - (a) forming a plasticizer/promoter phase comprising a primary plasticizer, a polyaminoamide – polyimidazoline adhesion promoter,
 - (b) blending said plasticizer/promoter phase with a finely – divided vinyl chloride polymer and a filler to make said plastisol composition characterized by the addition during step (a) to the plasticizer/promoter phase of an effective amount of a secondary plasticizer nonionic solvent effective in solvating said adhesion promoter in said plasticizer/promoter phase.
9. The method of claim 8 characterized in that said secondary plasticizer nonionic solvent ranges from between 10 to 70 weight parts per 100 weight parts of said vinyl chloride polymer.
10. The method of claim 8 characterized in that said primary plasticizer ranges from between 20 and 200 weight parts per 100 weight parts of said vinyl chloride polymer.
11. The method of claim 8 characterized in that said adhesion promoter ranges from between 1 and 10 weight parts per 100 weight parts of said vinyl chloride polymer.
12. The method of claim 8 characterized in that said secondary plasticizer nonionic solvent is selected from the group consisting of monoisopropyl biphenyl, diethylene glycol monoethyl ether, diisopropyl biphenyl, phenylxylyl ethane, butylated biphenyl, and mixtures thereof.
13. The method of claim 8 characterized in that it contains more than one of said vinyl chloride polymer.
14. The method of claim 8 characterized in that it additionally comprises a thixotropic agent ranging from between 1 and 5 weight parts per 100 weight parts of said vinyl chloride polymer.
15. A method for coating a metal substrate which comprises:
 - (a) applying a plastisol composition;
 - (b) applying an acid – catalyzed topcoat over said plastisol composition; and
 - (c) heating said coated metal substrate to cure said plastisol composition and said topcoat, characterized in applying as said plastisol composition, the plastisol composition of claims 1 – 7.
16. The method of claim 15 characterized in that said plastisol composition on said metal substrate is heated for its curing prior to applying said topcoat thereto.
17. The method of claims 15 and 16 characterized in that the proportion of secondary plasticizer ranges from between 10 and 70 weight parts, said primary plasticizer ranges from between 20 and 200 weight parts, and said promoter ranges from between 1 and 10 weight parts, all weight parts based on 100 weight parts of said vinyl chloride polymer.

Patentansprüche

1. Plastisol – Zusammensetzung, die ein feinverteiltes Vinylchlorid – Polymer, einen Füllstoff, einen Primär – Weichmacher und einen Polyaminoamid – Polyimidazolin – Haftvermittler enthält, wobei zum Überziehen des Plastisols mit einer Säure – katalysierten Deckschicht die Zusammensetzung eine Weichmacher/Vermittler – Phase aufweist, die den Primär – Weichmacher und den Haftvermittler enthält, dadurch gekennzeichnet, daß die Weichmacher/Vermittler – Phase zusätzlich eine wirksame Menge eines nichtionischen Sekundär – Weichmacher – Lösungsmittels enthält, das den Haftvermittler in der Weichmacher/Vermittler – Phase solvatisiert, wobei die Weichmacher/Vermittler – Phase zur Zugabe zu den restlichen Bestandteilen der Plastisol – Zusammensetzung vorgebildet wird.
2. Plastisol – Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das nichtionische Sekundär – Weichmacher – Lösungsmittel im Bereich zwischen 10 und 70 Gewichtsteilen pro 100 Gewichtsteile des Vinylchlorid – Polymers liegt.

3. Plastisol – Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß der Primär – Weichmacher im Bereich zwischen 20 und 200 Gewichtsteilen pro 100 Gewichtsteile des Vinylchlorid – Polymers liegt.
- 5 4. Plastisol – Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß der Haftvermittler im Bereich zwischen 1 und 10 Gewichtsteilen pro 100 Gewichtsteile des Vinylchlorid – Polymers liegt.
5. Plastisol – Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das nichtionische SekundärWeichmacher – Lösungsmittel aus der aus Monoisopropylbiphenyl, Diethylenglycolmonoethylether, Diisopropylbiphenyl, Phenylxylylethan, butyliertem Biphenyl und Gemischen davon bestehen –
10 den Gruppe ausgewählt ist.
6. Plastisol – Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß sie mehr als ein Vinylchlorid – Polymer enthält.
- 15 7. Plastisol – Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß sie zusätzlich ein thixotropes Mittel im Bereich zwischen 1 und 5 Gewichtsteilen pro 100 Gewichtsteile des Vinylchlorid – Polymers enthält.
- 20 8. Verfahren zur Herstellung einer Plastisol – Zusammensetzung, bei dem:
(a) eine Weichmacher/Vermittler – Phase gebildet wird, die einen Primär – Weichmacher und einen Polyaminoamid – Polyimidazolin – Haftvermittler enthält,
(b) die Weichmacher/Vermittler – Phase mit einem feinverteilten Vinylchlorid – Polymer und einem Füllstoff vermischt wird, um die Plastisol – Zusammensetzung herzustellen, gekennzeichnet durch
25 die Zugabe einer wirksamen Menge eines nichtionischen Sekundär – Weichmacher – Lösungsmittels, das den Haftvermittler in der Weichmacher/Vermittler – Phase solvatisiert, zur Weichmacher/Vermittler – Phase, und zwar während Schritt (a).
9. Verfahren nach Anspruch 8, dadurch gekennzeichnet, daß das nichtionische Sekundär – Weichmacher – Lösungsmittel im Bereich zwischen 10 und 70 Gewichtsteilen pro 100 Gewichtsteile
30 des Vinylchlorid – Polymers liegt.
10. Verfahren nach Anspruch 8, dadurch gekennzeichnet, daß der Primär – Weichmacher im Bereich zwischen 20 und 200 Gewichtsteilen pro 100 Gewichtsteile des Vinylchlorid – Polymers liegt.
- 35 11. Verfahren nach Anspruch 8, dadurch gekennzeichnet, daß der Haftvermittler im Bereich zwischen 1 und 10 Gewichtsteilen pro 100 Gewichtsteile des Vinylchlorid – Polymers liegt.
12. Verfahren nach Anspruch 8, dadurch gekennzeichnet, daß das nichtionische Sekundär – Weichmacher – Lösungsmittel aus der aus Monoisopropylbiphenyl, Diethylenglycolmonoethylether, Diisopropylbiphenyl, Phenylxylylethan, butyliertem Biphenyl und Gemischen davon bestehenden
40 Gruppe ausgewählt ist.
13. Verfahren nach Anspruch 8, dadurch gekennzeichnet, daß mehr als ein Vinylchlorid – Polymer enthalten
45 ist.
14. Verfahren nach Anspruch 8, dadurch gekennzeichnet, daß zusätzlich ein thixotropes Mittel im Bereich zwischen 1 und 5 Gewichtsteilen pro 100 Gewichtsteile des Vinylchlorid – Polymers enthalten ist.
- 50 15. Verfahren zum Beschichten eines Metallsubstrats, bei dem:
(a) eine Plastisol – Zusammensetzung aufgebracht wird;
(b) eine Säure – katalysierte Deckschicht auf die Plastisol – Zusammensetzung aufgebracht wird; und
(c) das beschichtete Metallsubstrat zur Härtung der Plastisol – Zusammensetzung und der Deckschicht erhitzt wird, dadurch gekennzeichnet, daß als Plastisol – Zusammensetzung die Plastisol –
55 Zusammensetzung nach den Ansprüchen 1 – 7 aufgetragen wird.
16. Verfahren nach Anspruch 15, dadurch gekennzeichnet, daß die Plastisol – Zusammensetzung auf dem Metallsubstrat zu ihrer Härtung erhitzt wird, und zwar vor dem Aufbringen der Deckschicht darauf.

17. Verfahren nach den Ansprüchen 15 und 16, dadurch gekennzeichnet, daß der Anteil des Sekundär-Weichmachers im Bereich zwischen 10 und 70 Gewichtsteilen, der des Primär-Weichmachers im Bereich zwischen 20 und 200 Gewichtsteilen und der des Vermittlers im Bereich zwischen 1 und 10 Gewichtsteilen liegt, wobei alle Gewichtsteile sich auf 100 Gewichtsteile des Vinylchlorid-Polymers beziehen.

Revendications

1. Composition de plastisol comprenant du polymère de chlorure de vinyle finement divisé, une matière de charge, un plastifiant primaire et un agent de polyaminoamide-polyimidazoline favorisant l'adhérence, dans laquelle, pour recouvrir ledit plastisol avec une couche de finition catalysée à l'acide, ladite composition comprend une phase plastifiant/promoteur comprenant ledit plastifiant primaire et ledit agent favorisant l'adhérence, caractérisé en ce que ladite phase plastifiant/promoteur comprend, en outre, une quantité efficace d'un solvant non ionique de plastifiant secondaire efficace pour solvater ledit agent favorisant l'adhérence dans ladite phase de plastifiant/promoteur, ladite phase de plastifiant/promoteur étant préformée pour y ajouter les ingrédients restants de la composition de plastisol.
2. Composition de plastisol selon la revendication 1, caractérisée en ce que ledit solvant non ionique de plastifiant secondaire se situe dans l'intervalle entre 10 et 70 parties en poids par 100 parties en poids dudit polymère de chlorure de vinyle.
3. Composition de plastisol selon la revendication 1, caractérisée en ce que ledit plastifiant primaire se situe dans le domaine entre 20 et 200 parties en poids par 100 parties en poids dudit polymère de chlorure de vinyle.
4. Composition de plastisol selon la revendication 1, caractérisée en ce que ledit agent favorisant l'adhérence se situe dans le domaine entre 1 et 10 parties en poids par 100 parties en poids dudit polymère de chlorure de vinyle.
5. Composition de plastisol selon la revendication 1, caractérisée en ce que ledit solvant non ionique de plastifiant secondaire est choisi parmi le groupe comprenant le biphenyle de monoisopropyle, l'éther monoéthylique de diéthylèneglycol, le biphenyle de diisopropyle, le phénylxylyléthane, le biphenyle butylé et des mélanges de ces derniers.
6. Composition de plastisol selon la revendication 1, caractérisée en ce qu'elle contient plus qu'un dudit polymère de chlorure de vinyle.
7. Composition de plastisol selon la revendication 1, caractérisée en ce qu'elle comprend, en outre, un agent thixotrope se situant dans le domaine entre 1 et 5 parties en poids par 100 parties en poids dudit polymère de chlorure de vinyle.
8. Procédé pour préparer une composition de plastisol, qui consiste à :
 - (a) former une phase plastifiant/promoteur comprenant un plastifiant primaire, un agent de polyaminoamide-polyimidazoline favorisant l'adhérence,
 - (b) mélanger ladite phase plastifiant/promoteur avec un polymère de chlorure de vinyle finement divisé et une matière de charge pour préparer ladite composition de plastisol, caractérisé par le fait que l'on ajoute, au cours de l'étape (a), à la phase plastifiant/promoteur, une quantité efficace d'un solvant non ionique de plastifiant secondaire efficace pour solvater ledit agent favorisant l'adhérence dans ladite phase plastifiant/promoteur.
9. Procédé selon la revendication 8, caractérisé en ce que ledit solvant non ionique de plastifiant secondaire se situe dans le domaine entre 10 et 70 parties en poids par 100 parties en poids dudit polymère de chlorure de vinyle.
10. Procédé selon la revendication 8, caractérisé en ce que ledit plastifiant primaire se situe dans le domaine entre 20 et 200 parties en poids par 100 parties en poids dudit polymère de chlorure de vinyle.

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11. Procédé selon la revendication 8, caractérisé en ce que ledit agent favorisant l'adhérence se situe dans le domaine entre 1 et 10 parties en poids par 100 parties en poids dudit polymère de chlorure de vinyle.
- 5 12. Procédé selon la revendication 8, caractérisé en ce que ledit solvant non ionique de plastifiant secondaire est choisi parmi le groupe comprenant le biphenyle de monoisopropyle, l'éther monoéthylique de diéthylèneglycol, le biphenyle de diisopropyle, le phénylxylyléthane, le biphenyle butylé et des mélanges de ces derniers.
- 10 13. Procédé selon la revendication 8, caractérisé en ce qu'elle contient plus qu'un dudit polymère de chlorure de vinyle.
14. Procédé selon la revendication 8, caractérisé en ce qu'elle comprend, en outre, un agent thixotrope se situant dans le domaine entre 1 et 5 parties en poids par 100 parties en poids dudit polymère de chlorure de vinyle.
- 15 15. Procédé pour l'enduction d'un substrat métallique, qui consiste à :
- (a) appliquer une composition de plastisol;
 - (b) appliquer une couche de finition catalysée à l'acide par-dessus ladite composition de plastisol;
 - 20 et
 - (c) chauffer ledit substrat métallique enduit pour durcir ladite composition de plastisol et ladite couche de finition, caractérisé en ce qu'on applique, à titre de ladite composition de plastisol, la composition de plastisol selon les revendications 1-7.
- 25 16. Procédé selon la revendication 15, caractérisé en ce que ladite composition de plastisol appliquée sur ledit substrat métallique est chauffée à des fins de durcissement avant de lui appliquer ladite couche de finition.
- 30 17. Procédé selon les revendications 15 et 16, caractérisé en ce que la proportion du plastifiant secondaire se situe dans le domaine entre 10 et 70 parties en poids, ledit plastifiant primaire se situe dans le domaine entre 20 et 200 parties en poids, et ledit promoteur se situe dans le domaine entre 1 et 10 parties en poids, toutes les parties en poids étant basées sur 100 parties en poids dudit polymère de chlorure de vinyle.

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